

1357 904

- (21) Application No. 18948/71 (22) Filed 4 June 1971  
 (31) Convention Application No. 50114 (32) Filed 10 June 1970 in  
 (33) Japan (JA)  
 (44) Complete Specification published 26 June 1974  
 (51) International Classification C08G 41/04 C08F 29/24  
 (52) Index at acceptance

C3R 32C11 32C12 32C13M 32C25 32C27 32C6X 32C8B  
 32C8P 32C8R 32D11A 32D1 32D9B1 32E2A 32EZY  
 32E9 32G2A 32G2Y 32H5B2 32H5BY 32J11  
 32J1A 32J1Y 32J2C 32J2F 32J2Y 32KH 32L2C1  
 32L6F  
 C3P 10C12B 10C12X 10C13A 10C17 10C20B 10D1A 10T2A



(54) PROCESS FOR PREPARING  
 POLYURETHANE-CONTAINING RESIN COMPOSITION

(71) We, KAO SOAP CO., LTD., of 7—18, 1-chome, Nihonbashi-Bakurocho, Chuo-Ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of a resin composition containing a finely divided, granular polyurethane resin.

The object of this invention is to provide a process which produces, at low cost, a polyurethane-containing resin composition having a granular form suitable for shaping or moulding in moulding machines, especially extrusion moulding machines, blow moulding machines and injection moulding machines. Another object of this invention is to provide a process which gives a polyurethane-containing resin composition which is not discolored and has not been subjected to long periods of heat treatment.

Since pulverisation of polyurethane is difficult, its development in obtaining polymer blends with other polymers has been retarded, though it is known that a resin composition of unique properties is obtainable by blending polyurethane with other polymers such as polyvinyl chloride. Polyurethane, especially polyester diol-diisocyanate adduct, exhibits an excellent compatibility with polyvinyl chloride and possesses a migration or extraction resistance comparable or superior to those of conventional polyester type plasticizers. Further, polyurethane can give an excellent impact resistance when mixed with polyvinyl chloride. However, since pulverisation of polyurethane is difficult, it is impossible to obtain a homogeneous mixture of polyurethane with powdery polyvinyl chloride. Accordingly, in the art there has been adopted a method comprising mixing and kneading polyurethane and polyvinyl chloride, and then cutting the mixture into pieces or granulating the mixture in an

extruder. However, this conventional technique is defective in that the number of process steps is increased and oxidation deterioration of polyurethane is brought about because it must be exposed to heat for a long time, resulting in discoloration of the end product, and that, in order to prevent this undesired discoloration, it is necessary to use a large amount of an expensive stabilizer and to change the type of colouring agent, resulting in a secondary problem of high manufacturing cost.

We have made researches with a view to developing a process for the preparation of a powdery or granular polyurethane-containing resin composition free of the above-mentioned defects, and in accordance with this invention, there is provided a process for the preparation of a thermoplastic mouldable resin composition, which comprises mixing (A) 100 parts by weight of particles or granules of a thermoplastic mouldable resin selected from polyvinyl chloride, vinyl chloride copolymers, chlorinated polyvinyl chlorides, polyamides, polyacrylonitrile, polymethyl methacrylate, synthetic rubbers, saturated polyesters and epoxy resin, with (B) a total of from 70 to 200 parts by weight of (1) a polyol component and (2) a polyisocyanate or a prepolymer having isocyanate groups at both ends of the molecule, at a temperature below the melt-adhesion temperature of the thermoplastic resin and effective to cause a polyurethane-forming reaction between components (1) and (2) to form polyurethane resin *in situ* on the thermoplastic resin particles.

The starting materials for producing polyurethane resin, namely components (1) and (2) are reacted in the presence of the thermoplastic resin to obtain a powdery or granular product suitable for shaping or moulding in the above-mentioned moulding machines, which product is composed of thermoplastic resin particles containing polyurethane on the surface and in the interior of the particles, or

[Price 25p]

of thermoplastic resin particles covered with polyurethane. In the process of this invention, the urethanisation reaction is completed on the surface of powder or granules of thermoplastic resin and particularly when polyvinyl chloride prepared by a suspension polymerisation process is used, since polyurethane can be contained within polyvinyl chloride powder or granules, there is obtained a non-tacky, dry blend of great adaptability.

In producing the above dry polymer blend of a polyurethane resin with a thermoplastic resin such as polyvinyl chloride resin, the ratio of the total weight of the starting materials for producing the polyurethane resin (polyol component plus polyisocyanate component) to the weight of, e.g. polyvinyl chloride powder or granules is generally in the range of 70—200 to 100, preferably 70—130 to 100.

Generally, the more the temperature at which the thermoplastic resin to be used in this invention becomes sticky or adhesive exceeds the urethanisation-initiating temperature, the easier it is to prevent adhesion among resin particles caused by the reaction heat. In addition to polyvinyl chloride as mentioned above, there may be used as the thermoplastic resin in the present invention vinyl chloride type resins such as vinyl chloride-vinyl ester copolymers, vinyl chloride-vinyl ether copolymers, chlorinated polyvinyl chlorides, vinyl chloride-vinyl acetate copolymers, vinyl chloride-vinylidene chloride copolymers, vinyl chloride-ethylene copolymers, vinyl chloride-propylene copolymers and vinyl chloride-ethylene-vinyl acetate terpolymers; polyamides, polyacrylonitrile resin, methyl methacrylate resins, polystyrene resin, synthetic rubbers such as butadiene-styrene copolymers and polyisoprenes; saturated polyesters; and epoxy resins. These thermoplastic resins are used in the finely divided form, namely in the granular or powdery form. The more highly porous the structure of the powdery or granular thermoplastic resin to be used, the more easily the polyurethane component can be contained in the interior of the particles of the thermoplastic resin and the better is the melt-adhesion among polyurethanised particles prevented. For instance, polyvinyl chloride prepared by suspension polymerisation gives better results than polyvinyl chloride prepared by emulsion polymerisation.

Particles or granules of the thermoplastic resin to be used in this invention include particles of a size, generally of 20 to 300 Tyler standard mesh, preferably 20 to 100 mesh, and pellets, the longest side of which is 1—10 mm, preferably 1—5 mm.

The polyol component to be used in this invention is selected from hydroxyl-terminated polyesters, hydroxyl-terminated polyethers, monomeric diols and mixtures thereof. Polyester diols may be prepared by ring-opening polymerisation of cyclic esters, polycondensa-

tion of diols with dibasic carboxylic acids, or any other conventional processes. As the diol component constituting the polyester diol there may be used ethylene glycol, propylene glycol, 1,3-propane diol, 1,4-butane diol, 1,5-pentane diol, 1,4-pentane diol, 1,3-pentane diol, 2,3-pentane diol, hexane diols, heptane diols and octane diols. The said diol component can be represented by the general formula  $R(OH)_2$ , wherein R is a straight or branched, saturated aliphatic hydrocarbon radical of 2 to 8 carbon atoms. As the dibasic carboxylic acid constituting the polyester diol there may be used oxalic acid, succinic acid, glutaric acid, adipic acid, pimelic acid and suberic acid. This dibasic acid component can be represented by the general formula  $R(COOH)_2$  wherein R is a saturated aliphatic hydrocarbon radical of 1 to 6 carbon atoms.

Typical examples of the polyesters or polyethers to be used in the present invention include polypropylene adipate, polybutylene adipate, polyhexamethylene adipate, polyoxytetramethylene glycol and polyoxypropylene glycol, each of which has a molecular weight of 300 to 3000, preferably 800 to 1200 and contains hydroxyl groups at both ends of the molecule. For instance, in combination with polyvinyl chloride, polyester diols are preferably used. In addition to the above-mentioned diols, there may be used polyols having three or more hydroxyl groups in the molecule. These polyols can be used as long as the resulting resin composition retains a thermoplastic property.

The isocyanate component in this invention includes both aromatic polyisocyanates and aliphatic polyisocyanates.

Typical examples of the isocyanates that can be suitably used include toluene diisocyanate, phenylene diisocyanate, diphenyl diisocyanate, diphenyl methane-p,p'-diisocyanate, diphenyl dimethyl methane diisocyanate, 1,5-naphthalene diisocyanate, phenylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate and hexamethylene diisocyanate.

It is known that, since commercially available diisocyanates generally have a low molecular weight and are volatile, the working efficiency is sometimes lowered by the smell and poisonous character of their vapours depending on the type of the manufacturing apparatus and that, in order to improve the physical properties of the polyurethane *per se*, it is convenient to add as the diol component a monomeric diol of a low molecular weight other than the above-mentioned polyester diols. In view of these facts, the use of a prepolymer having isocyanate groups at both ends, which may be prepared by reacting n moles of the above-mentioned diisocyanate with less than n moles of a monomeric diol or a polyester or polyether diol, may be sometimes advantageous, since the possibility of the above-men-

tioned lowering of the working efficiency can be removed.

In addition to the above-mentioned diisocyanates, polyisocyanates having 3 or more isocyanate groups in the molecule may be used likewise.

In the case when the polyisocyanate or polyol component is solid or highly viscous and, thus, the process is difficult to carry out, a diluent may be used. As the diluent there is preferably used a substance which is inert to the polyurethanisation reaction and can be included as one component in the resulting moulding resin composition. In the case of polyvinyl chloride, for instance, the use as the diluent of a plasticizer such as di-2-ethylhexyl phthalate is especially preferred. Such plasticizer does not inhibit the advance of the polyurethanisation reaction and acts as a plasticizer for polyvinyl chloride at the time of processing.

In this invention, the use of a urethanisation catalyst is not indispensable. Of course, in order to accelerate the reaction, it is possible to use a known urethanisation catalyst. For instance, dibutyl tin dilaurate or other dialkyl tin dialkanoates may be conveniently used when polyvinyl chloride is used as the thermoplastic resin component, because they act also as stabilisers for polyvinyl chlorides.

Other additives such as stabilisers and lubricants may be used. It is important that these additives are inert to the diisocyanate or at least substantially unreactive even if they have a reactivity. In other words, even if they have a reactivity with the diisocyanate, it must be much lower than the rate of the intended polyurethanisation reaction so that any reaction with the isocyanate does not occur to any significant degree. It is needless to say that no trouble will be brought about by the addition of an additive of a high reactivity if the addition is effected after completion of the urethanisation reaction.

It is desired that the reaction temperature be lower than the temperature at which bonding or melt adhesion of thermoplastic resin particles begins to occur. This is for the purpose of preventing the resin particles changing to a form not suitable for feeding them to a moulding machine, caused by melt adhesion of particles. When the thermoplastic resin particles react with a component other than said resin, for instance a plasticizer or stabilizer, prior to the polyurethanisation reaction, the reaction temperature is preferably lower than that at which the composition becomes sticky or melt-adhesion begins to occur. Ordinarily, this temperatures below 145°C, and preferably 100—140°C.

In order of addition of reactants, namely the diol component and the diisocyanate component is not critical in this invention, but the operation can be accomplished more easily when the diol component is at first absorbed

in thermoplastic resin particles and then the diisocyanate component is added thereto.

In the polyurethane-containing resin composition prepared according to this invention the polyurethane is distributed more uniformly than in a mixture formed by merely blending a polyurethane resin with an other thermoplastic resin, and there is no fear of phase separation between the polymers. Further, since the composition according to this invention takes a powdery or granular form suitable for feeding it to various conventional moulding machines, it can be conveniently used as the starting material for various moulded articles. For instance, it is suitably blow-moulded into bottles having an improved impact resistance and it is also suitable for the production of hoses and tubes where high migration or extraction resistance is required. The composition according to this invention is suitable for the manufacture of various other moulded articles.

This invention will now be described in detail by referring to the following examples.

In these examples, the effects of the present invention are explained with reference to typical embodiments of the invention by comparing them with conventional processes, but equivalent effects are obtainable when the process of this invention is practised with other combinations of components within the scope of the appended claims.

#### Example 1

10 g of cadmium stearate and 10 g of barium stearate were added to 1000 g of powder (about 48 Tyler mesh) of polyvinyl chloride of a degree of polymerisation of about 1450 prepared by suspension polymerisation and they were mixed by means of a Henschell type mixer. Then, 692 g of poly(1,3-butylene adipate) glycol having an average molecular weight of 1000 calculated from the number of the terminal hydroxyl groups was added to the mixture, and it was agitated for 10 minutes at 50—70°C. Then, 308 g of a prepolymer obtained by reacting 2 moles of 1,6-hexamethylene diisocyanate with 1 mole of 1,3-butylene glycol was added to the mixture and the resulting mixture was well blended. Then the mixture was heated and agitated for 30 minutes at 100—140°C. in a nitrogen current. Thus, there was obtained a powdery resin composition. A part of the composition was dissolved in dimethyl formamide at room temperature and subjected to infrared spectrum analysis. Any free isocyanate group was not detected by this analysis.

The above powdery resin composition was mixed for 10 minutes at a hot roll maintained at 150°C. and pressed for 5 minutes under a pressure of 100 kg/cm<sup>2</sup> by means of a hot press maintained at 160°C. Values of 100% modulus and elongation of the so formed sample were determined to be 65 kg/cm<sup>2</sup> and

500%. According to the Clash-Berg method (Ind. Eng. Chem., 34, 1218 (1942)), the flexible temperature  $T_f$  of the sample was measured to be  $-16^\circ\text{C}$ .

#### 5 Example 2

519 g of poly(1,4-butylene adipate) glycol and 40.7 g of 1,4-butylene glycol were added to 1000 g of powder (about 48 mesh) of polyvinyl chloride of a degree of polymerisation of about 800 prepared by suspension polymerisation, and the mixture was blended at  $140^\circ\text{C}$ . for 10 minutes by means of a 10-litre Henschell type mixer. Then, 245 g of diphenylmethane-4,4'-diisocyanate was added to the

mixture and it was blended at  $140^\circ\text{C}$ . for 20 minutes to form a powdery resin composition (Sample 1). Separately, polyvinyl chloride of a degree of polymerisation of 800 was mixed in the same manner above with an equal amount of a polyurethane elastomer, prepared by heating a mixture of the same starting materials as above for 3 hours at  $140^\circ\text{C}$ , and extruding into cubes to form a resin composition (Sample 2). When samples 1 and 2 were compared, it was seen, as shown below, that sample 1 exhibited greater tensile strength and elongation and was superior to Sample 2 with respect to adaptability for roll kneading operation and calender processability.

Sample No.	Product according to this invention	Comparative product
Stress in 100% elongation	1 225 kg/cm <sup>2</sup>	2 213 kg/cm <sup>2</sup>
Tensile strength	277 kg/cm <sup>2</sup>	242 kg/cm <sup>2</sup>
Elongation	235%	187%

#### Example 3

A powdery resin composition free of thermal discoloration was prepared by adding 519 g of poly(1,4-butylene adipate) glycol and 40.7 g of 1,4-butylene glycol to 1000 g of polyvinyl chloride of a degree of polymerisation of about 800 prepared by suspension polymerisation, mixing the resulting blend at  $140^\circ\text{C}$ . for 10 minutes by means of a 10-litre Henschell type mixer, adding to the mixture 167 g of toluene diisocyanate, and conducting the blending at  $120^\circ\text{C}$ . for 20 minutes.

#### Example 4

A 10-litre Henschell type mixer was charged with 1000 g of powder (about 48 Tyler mesh) of polyvinyl chloride prepared by suspension polymerisation, 700 g of poly(hexamethylene adipate) glycol and 63 g of 1,4-butylene glycol, and they were mixed together. Then 1 g of dibutyl tin dilaurate acting as both a catalyst for the urethanisation reaction and a stabilizer for polyvinyl chloride was added to the mixture, and the mixing was conducted at  $140^\circ\text{C}$ . for 10 minutes, followed by addition of 236 g of hexamethylene diisocyanate. The mixture was reacted at  $120^\circ\text{C}$ . for 20 minutes to form a polyurethane-containing, powdery resin composition free of thermal discoloration.

When the above procedure was repeated by employing powder of a vinyl chloride-vinyl acetate copolymer and powder of a vinyl chloride-vinylidene chloride copolymer instead of powder of polyvinyl chloride, there were obtained similar powdery resin compositions free of thermal discoloration.

#### WHAT WE CLAIM IS:—

1. A process for the preparation of a thermoplastic mouldable resin composition, which comprises mixing (A) 100 parts by weight of particles or granules of a thermoplastic mouldable resin selected from polyvinyl chloride, vinyl chloride copolymers, chlorinated polyvinyl chlorides, polyamides, polyacrylonitrile, polymethyl methacrylate, synthetic rubbers, saturated polyesters and epoxy resins, with (B) a total of from 70 to 200 parts by weight of (1) a polyol component and (2) a polyisocyanate or a prepolymer having isocyanate groups at both ends of the molecule at a temperature below the melt-adhesion temperature of the thermoplastic resin and effective to cause a polyurethane-forming reaction between components (1) and (2) to form polyurethane resin *in situ* on the thermoplastic resin particles.

2. A process according to Claim 1, in which said polyol component is selected from hydroxyl-terminated polyesters, hydroxyl-terminated polyethers, monomeric diols and mixtures thereof.

3. A process for the preparation of a thermoplastic mouldable resin according to claim 1 substantially as hereinbefore described with reference to the Examples.

WITHERS & ROGERS,  
Chartered Patent Agents,  
148—150 Holborn,  
London, EC1N 2NT.  
Agents for the Applicant.